Laboratory Name: Lawrence Livermore Nat. Lab.
B&R Code: KC020102

FWP and possible subtask under FWP:
Microstructural evolution and mechanical response of complex alloys under prolonged particle radiation

FWP Number: SCW0289

Program Scope:
New theoretical developments to firmly establish the physical basis of multi-field, quantitative Phase-Field Method (PFM) for simulations of microstructure evolution in irradiated materials. New computational algorithms for solving efficiently PFMs and related kinetic models. Experiments and atomistic calculations for both calibrating the model parameters relevant to specific alloys and testing key predictions such as the onset of microstructural instabilities under irradiation.

Major Program Achievements (over duration of support):
New Monte Carlo algorithm: Developed a computer code based on the new algorithm for diffusion Monte Carlo simulations based on the theory of first passage processes in 1D and demonstrated the speed-up of diffusion Monte Carlo simulations by several orders of magnitude.

Program Impact:
The new diffusion Monte Carlo code allows efficient simulations of defect microstructure including nucleation and ripening of defect clusters. This information will be passed on to the PFM code that is currently under development.

Interactions:
UIUC (R. Averback, P. Bellon and I. Robertson)
Stanford University (W. Cai)
MIT (S. Yip)
OSU (J. Li)

Recognitions, Honors and Awards (at least partly attributable to support under this FWP or subtask):
None.

Personnel Commitments for FY2005 to Nearest +/-10%:
V. Bulatov (40%)
G. Gilmer (40%)

Authorized Budget (BA) for FY05:
FY05 BA $300,000 (funded in July 2005)

Laboratory Name: Lawrence Livermore Nat. Lab.
B&R Code: KC020203

FWP and possible subtask under FWP:
CMSN – Microstructural Effects on the Mechanics of Materials

FWP Number: SCW0289

Program Scope: Development of a hierarchically structured, integrated approach towards materials modeling across the inherent physical length and time scales relevant to microstructural effects in materials mechanics. The specific goal is to elucidate the fundamental dislocation and grain-boundary processes responsible for the crossover from "normal" Hall-Petch behavior at larger grain sizes to the "inverse" behavior for smaller grain sizes (typically less than 20 nm).

Major Program Achievements (over duration of support):
Dislocation behavior: Discovered a so-far unrecognized mechanism of strain hardening in single crystals of BCC transition metals, the so-called dislocation multi-junctions.

Dislocation-grain boundary interactions: Elucidated a new mechanism of dislocation nucleation at the grain boundary through a zipping reaction among the grain boundary dislocations.

Ideal shear resistance: Obtained new data contradicting Frenkel's classic equation for the ideal resistance to shearing along rational crystallographic planes in defect-free crystals. Proposed new equations o describe the magnitude of the ideal shear resistance as a function of plane orientation.

Program Impact:
The unit mechanisms of dislocation-grain boundary interactions investigated within this subtask form the basis for further development of meso-scopic approaches to modeling the effects of material microstructure on the mechanical response. The results obtained over the years within this research sub-task provide key input for constructing accurate meso-scopic simulations of the mechanical strength of polycrystalline materials.

Interactions:
Carnegie Mellon University (Amit Achraya, Tony Rollettt)
Pacific Northwest National Laboratory (C. Henager and R. Kurtz)
Argonne National Laboratory (D. Wolf)
Stanford University (W. Cai)
MIT (S. Yip)
OSU (J. Li)
UIUC (I. Robertson)
M. de Koning (University of Campinas, Brazil)
R. Baran (RPI)

Recognitions, Honors and Awards (at least partly attributable to support under this FWP or subtask):
Lawrence Fellowship to Wei Cai (2001)
Defense & Nuclear Technology Directorate Award to V. Bulatov and W. Cai (2004)
8 Invited talks since 2001
Presidential Early Career Award for Scientists and Engineers (PECASE) to Wei Cai (2005)
Elected Fellow of the American Physical Society, V. Bulatov (2005) with the citation
"For outstanding contributions to computational materials sciences, particularly in the areas of dislocation dynamics and crystal plasticity"

Personnel Commitments for FY2005 to Nearest +/-10%:
V. Bulatov (10%)
W. Cai (5%)
R. Baran (15%)

Authorized Budget (BA) for FY03, FY04, FY05:
FY03 BA $39,000 **FY04 BA $**52,000 **FY05 BA $**52,000

Laboratory Name: LLNL
B&R Code: KC020101

FWP and possible subtask under FWP:
Complex Transient Events in Materials Studied Using Ultrafast Probes and Terascale Simulation
FWP Number: SCW0289

Program Scope:
We seek to study complex transient phenomena by applying ultrafast techniques to problems in materials science. The new technique of dynamic transmission electron microscopy (DTEM) has been identified as a potentially powerful technique to characterize and identify mechanisms in fast, dynamic events in materials. We plan to explore the atomic level mechanisms and structures in martensitic transformations in materials, specifically the pressure driven α to ε transformation in Fe and the temperature driven α to β transformation in Ti (and related systems).

Major Program Achievements (over duration of support):
We have achieved operation of the DTEM at LLNL for the conditions of 1.5 ns pulsed electron beam operation with 10^7 electrons per pulse. The specimen drive laser has been brought incident onto the specimen in order for it to be stimulated into the desired state. This treatment laser has a pulse duration of 80 ns FWHM and power up to several hundred mJ per pulse. We have used specimen drive pulses of a few μJ to heat specimens of Ti into the β phase field and observed their structural transformation with pulsed electron diffraction. We have demonstrated dynamical image contrast formation in the DTEM for the first time. We have also demonstrated a spatial resolution of approximately 20 nm in imaging mode.

Program impact:
We have commissioned an instrument that can perform electron diffraction experiments of TEM specimens being irradiated with a treatment laser with high spatial resolution and on the time scale of 1.5 ns. This capability has not existed before anywhere in the world.

Interactions:
Prof. Nigel Browning, University of California, Davis – DTEM studies of transient events in materials.
Prof. Peter Weber, Brown University – Ultrafast electron diffraction at MeV energy levels.
Prof. Harald Rose, TU Darmstadt – implications of pulsed operations on electron optical systems

Recognitions, Honors and Awards (at least partly attributable to support under this FWP or subtask):
Invited presentation for Dr. G.H. Campbell, at a NSF workshop at Arizona State University on "Dynamic *in situ* electron microscopy as a tool to meet the challenges of the nanoworld", Jan. 3 – 6, 2006.
Invited presentation for Dr. W.E. King at M&M: Wayne E. King, G. H. Campbell, Alan Frank1, Bryan Reed, John Schmerge, Brad Siwick, Brent Stuart, and Peter Weber Toward Ultrafast Electron Microscopy, Microscopy and Microanalysis Meeting July 31, 2004
Invited presentation for Dr. W.E. King at FEMMS2005: Wayne E. King, Michael Armstrong, Ken Boyden, Geoffrey H. Campbell, William DeHope, Alan Frank, Thomas LaGrange, Bryan Reed, Richard Shuttlesworth, Benjamin Pyke, and Brent Stuart Ultrafast Electron Microscopy and Diffraction, FEMMS2005 September, 26 2005

Personnel Commitments for FY2005 to Nearest +/- 10%:
Dr. G.H. Campbell (PI) (20%), Dr. T.B. Lagrange (post-doc) (100%), Dr. J.D. Colvin (staff scientist, laser/materials interactions) (20%), Ms. J.S. Kim (student) (100%)

Authorized Budget (BA) for FY03, FY04, FY05:
FY03 BA $274k **FY04 BA $274k** **FY05 BA $359k**

Laboratory Name: LLNL
B&R Code: KC020203

FWP and/or subtask Title under FWP: SCW0289
Semiconductor nanostructure by scientific design

FWP Number: SCW0289

Program Scope: Investigation of the structural, electronic, optical and mechanical properties affecting the scientific design of semiconductor nanostructures, by using the unique computational expertise and capabilities of Lawrence Livermore National Laboratory (LLNL). The focus is on the science of quantum dots and nanorods, in particular on the use of *ab initio* simulation techniques to unravel the effects of different surface structures and passivation on the properties of semiconductor nanoparticles. The main goal is to establish an effective scientific paradigm for designing semiconductor nanostructures on the atomic scale.

Major Program Achievements (over duration of support):
Completed an investigation of the structural, electronic and optical properties of hydrogen-passivated silicon nanowires with different growth directions in the range of 1 to 3 nm in diameter. Results of this work have been submitted for publication in *Phys. Rev. B.*
Completed a study of the structural and optical properties of nanodiamonds up to 3 nm in size. Results published in J. Elect. Chem, PRL and CPC.

Raty, J.Y. and G. Galli, Optical properties and structure of nanodiamonds, J. Elect. Chem. 584, 9 (2005); Drummond, N.D., A.J. Williamson, R.J. Needs and G. Galli, Electron emission from diamondoids: A diffusion quantum Monte Carlo study, Phys. Rev. Lett. 95, 096801 (2005); Raty, J.Y. and G. Galli, First principle study of nanodiamond optical and electronic properties, Comp. Phys. Comm. 169, 14 (2005)

Program Impact:
Provided insight into the physical and chemical properties of semiconductor quantum dots and into the growth mechanism of nanorods. Provided the first *ab initio* simulations able to efficiently describe d-electron systems in dots with more than 90 atoms.

Interactions:
University of California Berkeley (P. A. Alvisatos, L. Manna)
University of Illinois at Urbana Champaign (Richard Martin)
University of North Carolina (Lubos Mitas)
University of Cambridge England (Richard Needs)
MIT (Nicola Marzari)

Recognitions, Honors and Awards (at least partly attributable to support under this FWP or subtask):
2004 LLNL Science and Technology Award (Galli, Williamson and Grossman)
More than 20 invited talks.
High profile publications

Personnel Commitments for FY2005 to Nearest +/-10%:
Giulia Galli (25%)
Andrew Williamson (20%)

Authorized Budget (BA) for FY03, FY04, FY05:
FY03 BA $200,000 **FY04 BA** $400,000 **FY05 BA** $180,000

Laboratory Name: Lawrence Livermore National Lab

B&R Code: KC020301

FWP and/or subtask Title under FWP: Electron Correlation in Complex Systems

FWP Number: SCW0289

Program Scope: We are developing and using photon dichroic and spin resolved techniques to investigate complex materials and do world-class science. These materials include potential spintronic device sources such as half-metallic ferromagnetic materials and correlated electronic materials such as non-magnetic δ-Pu, which appears now to have a novel internal spin and orbital polarization in its valence band structure.

Major Program Achievements (over duration of support):

Publications since last report in Nov 2004.

1. J.G. Tobin, K.T. Moore, B.W. Chung, M.A. Wall, A.J. Schwartz, G. van der Laan, and A.L. Kutepov, "Competition Between Delocalization and Spin-Orbit Splitting in the Actinide 5*f* States," Phys. Rev. B 72, 085109 (Aug 15, 2005).
2. J.G. Tobin, B.W. Chung, J. Terry, R. K. Schulze, J. D. Farr, K. Heinzelman, E. Rotenberg, and D. K. Shuh, "Synchrotron Radiation-based Investigations of the Electronic Structure of Pu," Proceedings of the Russian Pu Workshop, August/September 2004, Sarov, Russia, Materialovedenie 5, 11 (May 2005).
3. M. Spangenberg, J.R. Neal, T.H. Shen, S.A. Morton, J.G. Tobin, G.D. Waddill, J.A.D. Matthew, D. Greig, A.E.R. Malins, E.A. Seddon, M. Hopkinson, "Observation of a low Curie temperature ferro-magnetic phase of ultrathin epitaxial Fe films on GaAs (001)," J. Mag. Mag. Matl. 292, 241 (April 2005).
4. J. Tobin and D. Shuh, "Actinide Spectroscopy Workshop," Syn. Rad. News, 18, 9 (March 2005).
5. A. P. Holm, T. C. Ozawa, S. M. Kauzlarich; S. A.Morton; G. D. Waddill; and J. G. Tobin, "XPS Studies of Yb14MnSb11 and Yb14ZnSb11, Solid State Chem. 178, 262 (2005).
6. J.G. Tobin, B. Chung, J. Terry, R. K. Schulze, J. D. Farr, K. Heinzelman, E. Rotenberg, and D. K. Shuh, "X-ray Absorption and Photoelectron Spectroscopy of Pu at the Advanced Light Source: Sample Quality Analysis," Proceedings of the Actinide XAS Meeting, Berkeley, CA; September 14-16, 2004, OECD Nuclear Energy Agency (NEA, France), accepted April 2005.
7. J.G. Tobin, K.T. Moore, B.W. Chung, M.A. Wall, A.J. Schwartz, G. van der Laan, and A.L. Kutepov, "A Study of the Competition Between Delocalization and Spin-Orbit Splitting in the Actinide 5*f* States," in "Recent Adv. in Act. Sci.," Proc. of the Actinides 2005 Mtg, Manchester, UK, accepted Aug 05.
8. K.T. Moore, G. van der Laan, J.G. Tobin, B.W. Chung, M.A. Wall, and A.J. Schwartz, "Probing the Population of the Spin-Orbit Split Levels in the Actinide 5*f* States," UltraMicroscopy, accepted Aug 05.

International Invited Talks since last report in Nov 2004:

1. J.G. Tobin, "Spin and orbital polarization; the key to explaining the unusual behavior of Pu and the actinides," Strongly Correlated Electron Systems (SCES) Mtg, Vienna, Austria, July 25-30, 2005.

Program impact:

Sixty years after its discovery by E.O. Lawrence, the mystery of the electronic structure of Pu is finally being resolved. In a series of experiments and linked theoretical modeling, the range of possible solutions for Pu electronic structure has been dramatically reduced. We have demonstrated the following with respect to the electronic structure of Pu: (1) the 5*f* spin orbit splitting is large (not Russell Saunders); (2) the number of Pu 5*f* electrons is five; (3) the spin orbit splitting dominates the dispersion or delocalization in the 5*f* states. Our PRB of August 2005 is a crucial experimental benchmarking of the electronic structure of Pu. Delocalization of the Pu 5*f* states is a secondary (or possibly tertiary) effect. Moreover, we are now developing a new paradigm to explain the electronic structure of Pu, based upon the observation of strong *jj*-skewed spin orbit splitting and the possibility of spin and orbital polarization in the 5*f* valence bands of non-magnetic Pu. We are pursuing Double Polarization Photoelectron Dichroism measurements, using spin resolving detection in photoelectron spectroscopy, to test our hypothesis. We are also working to test various potential pure-spin electronic sources for spintronic devices, both at the ALS (Berkeley) and the APS (Argonne), using high energy spin resolved photoelectron spectroscopy.

Interactions: USA- National Labs: LBNL-D.K. Shuh; LANL-R. K. Schulze, J. D. Farr. USA-Universities: UMR-G.D. Waddill, T. Komesu; UCD-A.P. Holm, S.M. Kauzlarich, T. C. Ozawa;. International: A.L. Kutepov (VNIITF, Snezhinsk, Russia); G. Van der Laan (Daresbury Lab, UK); M. Spangenberg, J.R. Neal, T.H. Shen, J. Matthew, D. Greig, A. Malins, E.A. Seddon, M. Hopkinson (UK).

Personnel Commitments for FY2006 to Nearest +/- 10%:

J.G. Tobin (PI): 10%; S.W. Yu (Postdoc): 50%; B.W. Chung: 5 %; T. Komesu (PD,UMR) 100%

Authorized Budget (BA) for FY03, FY04, FY05:

FY03 BA $350,000 **FY04 BA** $341,000 **FY05 BA** $315,000

Laboratory Name: Lawrence Livermore
B&R Code: KC020301

FWP and/or subtask Title under FWP:
Manipulation and Quantitative Interrogation of Nanostructures (Formally Known As: Advanced Heterointerfaces)

FWP Number: SCW0289

Program Scope:
The goal of the advanced interfaces project is the characterization of the surface, geometric and electronic structure of nanostructured material using synchrotron radiation. By measuring the change in band edges as a function of particle size, surface termination and particle interaction we are able to get a measure of the true electronic structure in real nanoscale systems. These measurements are compared directly with first principles calculations to interpret for the first time how structure and local environment affect the properties of these nanoscale materials.

Major Program Achievements (over duration of support):
The majority of theoretical investigations on quantum confinement effects have been performed on isolated particles with idealized structures and surface terminations. In contrast, experimental systems researched so far exhibit either a size distribution, or possess ill-defined surface reconstruction or termination. Now, with the isolation of diamondoids a new class of clusters allows a study of quantum confinement in the molecular size limit. The first diamondoid, adamantane, consists of the smallest possible single cage unit excised from the diamond lattice, with each dangling bond terminated by hydrogen atoms. Each subsequent diamondoid adds one additional face-fused cage giving a perfectly size selected hydrogen terminated cluster in the bulk lattice configuration. Size dependent changes in the conduction band of individual diamond clusters in the gas phase were investigated by means of carbon K-edge x-ray absorption spectroscopy in ion yield mode. Comparison of the carbon K-edge absorption data for the series from adamantane (one diamond cage) to hexamantane (six diamond cages) with a bulk diamond crystal reference unveils interesting trends. The observed non-shifted absorption onset is further evidence for a special role of diamond within the group IV semiconductors. While earlier x-ray absorption measurements on deposited Si and Ge nanocrystals showed clear blue shifts of the conduction band minimum due to quantum confinement no such shifts could be measured for diamondoids or 4 nM nanodiamonds. This is in contrast to theoretical investigations of diamond clusters which predict increasing band gaps for decreasing sizes only below one nanometer. Depending on the calculations, the predictions show contradictory results, with either significant or no blue shift of the lowest unoccupied density of states. The theoretical models, however, do not appropriately predict the observed additional density of states below the bulk absorption onset due to the hydrogen surface. These specific states, which have been observed for the first time, effectively reduce the overall particle gap. The present experiments show that the hydrogen surface atoms have a significant impact on the overall electronic structure of the diamond clusters to a degree where they dominate the absorption onset and thus lowest unoccupied states.

Program Impact:
We are the first to measure the electronic structure of a monodispersed perfectly terminated quantum dot system. These perfectly match the theoretical model of an ideal isolated cluster.

Interactions:
UC- Santa Cruz, J. Zhang; Max-Plank-Institut Fur Mikkrostruckturphysik, Margit Zacharias; Florida State University, G. F. Strouse; Sandia National Laboratory , J. Wilcoxson; Chevron Texaco Richmond Plant, J. Dahl.

Recognitions, Honors and Awards (at least in some part attributable to support under this program):
LJT named fellow of the APS.
12 invited talks to international and national meetings.

Personnel Commitments for FY2004 to Nearest +/- 10%:
L. Terminello 10% T. van Buuren (staff scientist) 30% R. Meulenberg (post-doc) 30% A. Montoya Vaverka (student) 50%

Authorized Budget (BA) for FY03, FY04, FY2005:
FY03: BA 350,000 **FY04 BA: 340,000** **FY05 BA: 315,000**